

# PATENT SPECIFICATION

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## (54) DETERGENT BARS

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent bars.

The invention provides detergent bars intended for conventional toilet soap uses, either as hand soaps or bath or shower soaps, which are elastic in nature, giving them unusual tactile properties, such as "squeezability", which makes them like a plaything for children, thereby helping to make bathing more pleasant. The invention also includes a method for manufacturing such elastic detergent bars.

In accordance with the present invention an elastic detergent bar comprises synthetic organic detergent, gelatin and a liquid medium which is water and/or lower pluralhydric alcohol (namely a dihydric or lower polyhydric alcohol containing not more than 6 carbon atoms and not more than 6 hydroxyl groups per molecule); a cross linking agent and/or a denaturing agent for the gelatin being present at least when the synthetic organic detergent (including soap) present is solely an anionic detergent and the liquid medium is aqueous.

Within the generality of the invention there are several aspects or divisions.

In one form of the first of these aspects are elastic detergent bars comprising anionic detergent (as the sole synthetic organic detergent present), gelatin, a cross-linking agent and/or a denaturing agent for the gelatin and as the liquid medium, water or a mixture of water and lower pluralhydric alcohol, preferably only water. In another form of the first aspect of the invention the synthetic detergent comprises an amphoteric synthetic organic detergent and the liquid medium is water or a mixture of water and lower pluralhydric alcohol, preferably only water. When an amphoteric synthetic organic detergent is utilized a cross-linking agent may be present or, often preferably, may be omitted. In some embodiments of these first aspects of the invention the elastic detergent bar is one wherein the synthetic organic detergent is an anionic or an amphoteric synthetic organic detergent, the gelatin is a Type A gelatin of 100 to 300 g Bloom, a cross-linking agent and/or a denaturing agent is (or are) present, which cross-linking agent is a salt of aluminium, calcium, magnesium or zinc and which denaturing agent is urea, and the liquid medium is water, the percentages of components being from 10% to 80% of synthetic organic detergent, from 5% to 30% of gelatin, from 0.1% to 5% of cross-linking agent and/or denaturing agent, and from 5% to 60% of water.

All percentages and other proportions in this specification are by weight.

In the second aspect of the invention, a mixture of anionic and amphoteric synthetic organic detergents is employed, usually being from 10% to 80% of the elastic detergent bar, in a proportion in the range from 1:5 and 5:1, and with from 5% to 30% of gelatin and from 5% to 60% of water also present. In such bars the amphoteric synthetic organic detergent is preferably an imidazolinium betaine or a betainodipropionate, the proportion of anionic to amphoteric synthetic organic detergent is preferably in the range from 1:4 to 2:1 and the gelatin is preferably a Type A gelatin of from 100 to 300 g Bloom. In more highly preferred bars the amphoteric synthetic organic detergent is triethanolammonium 1-carboxy-methyl-1-

carboxyethoxyethyl-2-coco-imidazolinium betaine, the gelatin is of 200 to 300 g Bloom, from 3% to 20% of lower pluralhydric alcohol, such as glycerol or propylene glycol, is included and the proportions of the other components are from 35% to 70% of synthetic organic detergents, from 7% to 25% of gelatin and from 10% to 40% of liquid medium.

5 In a third aspect of the invention the elastic detergent bar includes sufficient gas in small bubbles distributed throughout so that the density is in the range from 0.5 to 0.98 g/cc. It has been found that such distributed gas significantly improves the stability of the elastic detergent bar on storage at elevated temperatures. In such detergent bars the detergent component is preferably a mixture of anionic and amphoteric synthetic organic detergents in a proportion in the range from 1:5 to 5:1 and the gas is air, the proportions of detergent, gelatin and water being from 20% to 80%, from 5% to 30% and from 5% to 50%, respectively. Preferably the anionic synthetic organic detergent is an alkali metal higher fatty monoglyceride sulphate, an ammonium higher fatty monoglyceride sulphate or a triethanolammonium higher fatty alcohol sulphate or a mixture of any of these; the amphoteric detergent is an imidazolinium betaine, a betaminodipropionate or a mixture thereof; the proportion of anionic detergent to amphoteric detergent is in the range from 1:3 to 3:1, the gelatin is a Type A gelatin of 100 to 300 g Bloom; and the density of the bar is in the range from 0.64 to 0.9 g/cc.

The fourth aspect of the invention provides a product of improved form retaining ability and foaming power and which comprises a deterative quantity of synthetic organic detergent, a gelling and bodying content of gelatin and sufficient lower pluralhydric alcohol to act as a solvent and gelling medium for the detergent and gelatin, in such proportions as to produce a solid elastic detergent bar essentially free or completely free of water. Preferably, the synthetic organic detergent is an ammonium or lower alkanolammonium anionic synthetic organic detergent or a mixture thereof with an amphoteric synthetic organic detergent, and the proportions of detergent, gelatin and lower pluralhydric alcohol are from 10% to 70%, from 8% to 35% and from 20% to 65%, respectively. In a more preferred composition the synthetic detergent is an anionic synthetic organic detergent, the gelatin is Type A gelatin of 100 to 300 g Bloom and the pluralhydric alcohol is a mixture of glycerol and propylene glycol in a ratio in the range from 5:1 to 1:2.

30 The elastic detergent bars embodying the invention may be manufactured by heating a mixture of the specified components, during which heating some or all of the water, if present, may be evaporated off, following which the mixture is formed into a bar, preferably by moulding and cooling.

35 Thus according to the method mode of the invention, a method for manufacturing an elastic detergent bar comprises heating a mixture of a synthetic organic detergent, gelatin, a liquid medium which is water and/or lower pluralhydric alcohol, and, at least when the synthetic organic detergent is solely an anionic detergent and the liquid medium is aqueous, a cross-linking agent and/or a denaturing agent for the gelatin, and, when water is present in the liquid medium, evaporating off a proportion of the water while the mix is in the liquid state, and forming the bar.

40 When air or other gas is to be included it maybe mixed in with the rest of the mixture while the latter is still in the liquid state and thick enough to hold the gas, and dispersed therein, and the mix is moulded and cooled rapidly enough to avoid the air forming larger bubbles. When, instead of water being present in the final product, a lower pluralhydric alcohol, such as a mixture of propylene glycol and glycerol, is to be present, if any water is initially in the mix it may be evaporated off with heat and/or vacuum before the final moulding, or water may be omitted entirely from the manufacturing procedure.

45 The anionic synthetic organic detergents which may be utilized in performing this invention include sulphates, sulphonates and phosphonated hydrophobic moieties, especially those which include higher hydrocarbyl groups (preferably fatty), such as alkyl groups of 8 to 20 carbon atoms, preferably of 10 to 18 carbon atoms. These compounds are usually employed as their water-soluble salts, such as salts of alkali metals, e.g. sodium and potassium, and triethanolamine and ammonia. These salts will usually be sodium, potassium or triethanolamine salts and of these the triethanolamine (or triethanolammonium or TEA) salts will often be preferred. Among the various types of synthetic anionic organic detergents which may be useful are the linear higher alkylbenzene sulphonates, especially those of 12 to 15 carbon atoms, e.g., sodium linear tridecylbenzene sulphonate; paraffin sulphonates; olefin sulphonates; higher fatty alcohol sulphonates; monoglyceride sulphates, especially the sulphated monoglycerides of coconut oil, tallow, hydrogenated coconut oil, hydrogenated tallow and synthetic higher fatty acids of 8 to 20 carbon atoms, e.g., sodium coconut oil monoglyceride sulphate, ammonium cocomonoglyceride sulphate; corresponding sulphates and phosphonates and other equivalent organic sulphonates, in most of which the lipophilic group includes a chain of 10 to 18 carbon atoms. Additionally useful are the sulphates and sulphonates of nonionic detergents and of nonionic surface active agents, in which products the nonionic base will normally be a polyethylene oxide condensation product of a higher fatty

alcohol, such as a condensation product based on a higher fatty alcohol of 10 to 18 carbon atoms, wherein the ethylene oxide content is from 3 to 30, preferably 5 to 10 or 12 mols of ethylene oxide per mol of higher fatty alcohol. A specifically preferred anionic detergent is ammonium monoglyceride sulphate of 8 to 18 or 20 carbon atoms in the fatty acid group, e.g., ammonium cocomonoglyceride sulphate (coco indicates derivation of the fatty acids from coconut oils), although alkali metal monoglyceride sulphates, such as sodium monoglyceride sulphate, are also useful. While sodium lauryl sulphate is an anionic synthetic organic detergent which may be employed, preferably in minor proportion with other anionic synthetic organic detergents in the present compositions, its use is usually not as preferable and the corresponding triethanolammonium salt is normally used instead because it produces a bar of good washing and foaming ability which is also stable on storage and maintains its elasticity during use. The ammonium and tri-lower alkanolammonium salt detergents also aid in making a clear product, rather than a cloudy one, which often results when metal salts, such as alkali metal salts, are used, and it is usually considered to be more desirable for the present detergent articles to be clear.

The amphoteric detergents which may be utilized to manufacture the elastic detergent bars of this invention include such compounds as Deriphat 151, which is sodium N-coco-betaaminopropionate (manufactured by General Mills, Inc.—DERIPHAT is a trade mark) and other betaaminopropionates and betaminodipropionates, such as sodium N-lauryl betaminodipropionate, Miranol C<sub>2</sub>M (anhydrous acid form, 1-carboxymethyl-1-carboxyethoxyethyl-2-coco-imidazolinium betaine-MIRANOL is a trade mark), the water soluble salts thereof, especially the triethanolammonium salt, and other imidazolinium betaines, and other of the various known amphoterics, described in McCutcheon's *Detergents and Emulsifiers*, 1973 Annual and in *Surface Active Agents*, Vol. II, by Schwartz, Perry and Berch (Interscience Publishers, 1958). For example, Deriphats 151C, 154, 160, 160-C and 170-C, and Miranols C<sub>2</sub>M, S<sub>2</sub>M and SHD Conc. may be employed. Additionally, even liquid amphoteric detergents may be used, at least in part, e.g., up to 25 or 50% of the total amphoteric detergent content. The recited references also contain extensive descriptions of various suitable anionic detergents and of nonionic and cationic detergents which may be employed in small proportion(s) in the present compositions. The various long chain substituents in the mentioned amphoterics are of 8 to 20 carbon atoms, preferably of 10 to 18 carbon atoms and most preferably are lauryl and coco.

The nonionic detergents, while not required components of the invented products, may be present in relatively small proportions therein in replacement of some of the anionic or amphoteric detergents. The nonionics are preferably solid or semi-solid at room temperature, more preferably solid, and include but are not limited to ethoxylated aliphatic alcohols having straight or branched chains (preferably straight chain) of from 8 to 20 carbon atoms, with from 3 to 30 ethylene oxide units per molecule. Particularly suitable nonionic detergents of such type are manufactured by Shell Chemical Company and are marketed under the trademark Neodol. Of the various Neodols available, Neodol 25-7 (12-15 carbon atoms chain higher fatty alcohol condensed with an average of 7 ethylene oxide units per mol) and Neodol 45-11 (14-15 carbon atoms chain higher fatty alcohol condensed with an average of 11 ethylene oxide units per mol) are particularly preferred. Another suitable class of ethoxylated aliphatic alcohol detergents is made by Continental Oil Company and is sold under the trademark Alfonic. Of the Alfonic's the most preferred is Alfonic 1618-65, which is a mixture of 16 to 18 carbon atoms primary alcohols ethoxylated so as to contain about 65 mol percent of ethylene oxide. Additional examples of nonionic synthetic organic detergents include those marketed by BASF Wyandotte under the trademark PLURONIC. Such compounds are made by condensation of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol. The hydrophobic portion of the molecule has a molecular weight of from about 1,500 to about 1,800 and the addition of polyoxyethylene (or ethylene oxide) to such portion increases the water solubility of the molecule as a whole, with the detergent being a solid at room temperature when the polyoxyethylene content is about 50% of the total weight of the condensation product. Such a nonionic detergent is Pluronic F-128 but Pluronic F-68 may also be employed. Also useful nonionic detergents are the polyethylene oxide condensates of alkyl phenols, such as the condensation products of such compounds wherein the alkyl group contains from 6 to 12 carbon atoms, in either a straight chain or branched chain configuration, with 5 to 25 mols of ethylene oxide per mol of alkyl phenol. The alkyl substituents in such compounds may be derived from polymerized propylene or may be diisobutylene, octene or nonene, for example.

Representative cationic detergents, which usually also possess antibacterial (and fabric softening) properties, include di-higher alkyl di-lower alkyl ammonium halides, such as distearyl dimethyl ammonium chloride, and 2-hepta-decyl-1-methyl-1-[2-stearoylamido]ethyl-imidazolinium methyl sulphate. The higher alkyls thereof are of 8 to 20 carbon atoms, preferably 12 to 18 and the lower alkyls are of 1 to 4 carbon atoms, preferably 1

or 2. Such materials are normally omitted from anionic detergent-based products but may be employed in small proportions in amphoteric-based elastic detergent bars.

5 Gelatin, a complex mixture of collagen degradation products of molecular weight in the range of about 30,000 to about 80,000 and higher, depending on the hydrolytic conditions to which it has been subjected, is a vital constituent of the present compositions. Apparently 5 because of its outstanding ability to form reversible gels, its high viscosity and the excellent strengths of films thereof, it helps to make an elastic detergent bar which is of satisfactory strength and cleaning power, due to gradual dissolution of the ordinarily extremely soluble synthetic organic detergent component, and yet, which does not produce objectionable and 10 unacceptable soft gels at bar surfaces after they have been moistened. Additionally, and a major advantage of the present invention, the combination of gelatin and synthetic organic detergent, in the presence of water and preferably also in the presence of a lower dihydric or polyhydric alcohol or other suitable plasticizer or co-solvent, and in the case of anionic synthetic organic detergents alone, in the presence of a cross-linking agent and/or a 15 denaturant, yields elastic products. The elastic detergent bars made are sufficiently elastic so that a bar 2 cm. thick can be wetted and pressed between thumb and forefinger to a 1 cm. thickness and will immediately (at the most within five seconds) return to the 2 cm. thickness or at least to within about 1 mm. thereof, upon pressure release.

The gelatin employed is essentially colourless and free from odour. It is amphoteric (about 20 45 milliequivalents of amino functions and about 70 milliequivalents of carboxyl functions per hundred grams thereof). In formulating the present bars it is normally used as a dry granular product which is crystalline in appearance although it is really amorphous. It is insoluble in cold water but swells rapidly in the presence of water until it has imbibed from about 6 to about 8 times its weight thereof and it melts to a viscous solution in water when warmed to 40 to 45°C. 25 or more. Gelatins are classified as either Type A or Type B, the former being from acid-cured stock, with an isoelectric point of from 8.3 to 8.5 and the latter being of alkali-cured stock, with an isoelectric point of from 4.8—5.0. Type A gelatins are preferred for the present applications but Type B gelatins may also be used, as may be mixtures of the two. The gelling 30 powers of gelatins are normally measured by the Bloom test. Often too, viscosity will also be employed to characterize a gelatin and a gel strength: viscosity ratio may be specified, e.g., 3:1 to 5:1. Gel strengths will range from 100 to 300 g. Bloom but will usually be in the range from 150 or 200 to 300, with gelatins of Bloom values of 225 g. and 300 g. being employed in the examples herein. The Type A gelatins will generally be utilized with the usual detergent bar constituents, normally intended for employment in neutral or slightly basic aqueous media 35 and the Type B gelatins will be preferred when acidic conditions are expected to be encountered (the present examples include mostly Type A).

Cross-linking agents for gelatin and for other proteins are metal salts which cross-link various gelatin molecules, apparently by reacting with free carboxyl functions thereof. This class of compounds is well known and the salts employed are usually those of aluminium, 40 calcium, magnesium and/or zinc that are soluble in aqueous media. In such salts the preferred anions are chloride, bromide, iodide, sulphate, bisulphate and acetate but other suitable anions may also be included. Examples of such salts include potassium aluminium sulphate hydrate [potassium alum,  $\text{KA}(\text{SO}_4)_2 \cdot 12\text{-H}_2\text{O}$ ], aluminium chloride, other alums, calcium chloride, magnesium sulphate and zinc acetate. Also useful for cross-linking is formaldehyde, 45 usually as formalin. 0.1 To 1% of formaldehyde is normally adequate. Although the presence of a cross-linking agent is often highly desirable in the formulations of the invented bar compositions, especially those based on anionic detergents alone, it has been found that such are not needed and sometimes are intentionally omitted from detergent bars in which amphoteric detergents are the major or sole deterative components.

50 Instead of or in addition to a cross-linking agent a denaturant may be employed with the gelatin of the present compositions. Such a compound also helps to reduce the solubility of gelatin at and near its isoelectric point and inhibits crystallization. Although denaturation may be effected by various materials, including various detergents, ethanol, acetone, strong acids and strong alkalis, chemical denaturation, such as by urea, dextrose or guanidine hydrochloride, is preferred and of these compounds urea is much preferred. Both cross- 55 linking and denaturation and the combination thereof are helpful in producing a lastingly elastic detergent bar of desired properties, suitable for repeated and satisfactory cleaning applications.

The lower pluralhydric alcohol component(s) of the present bars function(s) as a solvent 60 and plasticizer for the bar components, especially the gelatin. It facilitates solubilization of the detergent at a desired rate and maintains the surface of the bar soft. If the bar became objectionably hard at portions thereof this could be cause for rejection of it by consumers. Such alcohol also helps to distribute the various components evenly throughout the bar or cake. Although a variety of lower pluralhydric alcohols may be employed, including various 65 sugars and sugar alcohols having up to 6 carbon atoms and up to 6 hydroxyls per molecule, the

most preferred are those of 2 to 3 carbon atoms and 2 to 3 hydroxyl groups per molecule. Such compounds include propylene glycol (1,2-dihydroxypropane or 1,2-propylene glycol), trimethylene glycol (1,3-propylene glycol) and glycerol, of which 1,2-propylene glycol, glycerol and mixtures thereof are preferred. Other useful solvents are sold as Cellosolves, which are mono- and di-lower alkyl ethers of ethylene glycol (CELLOSOLVE is a trade mark). Additionally, sometimes monohydric alcohols, such as ethanol, are useful, primarily as supplementary solvents.

The water employed is preferably deionized water which will normally contain less than 10 parts and preferably less than 1 part per million of hardness, as calcium carbonate, but normal city waters may also be utilized, such as those having hardnesses in the range of 10, 20 or 50 to 150 or 300 p.p.m., as  $\text{CaCO}_3$ .

When a gas is dispersed in the elastic detergent bars to improve the stability of the bars at elevated temperatures it will preferably be air but also useful are various other gases such as nitrogen and argon and in some applications lower hydrocarbons, carbon dioxide, oxygen and lower chlorofluorohydrocarbons may also be employed. Thus, although, for example, carbon dioxide is somewhat soluble under the conditions of manufacture it may be sufficiently insoluble to be useful. The gas will usually be in microscopic bubble form with diameters often in the 1 micron to 1 mm. range, preferably 10 microns to 0.1 mm.

With the basic elastic detergent bar composition there may be present various adjuvant materials in minor proportions to contribute their particular properties to the final product. Among such adjuvant materials are functional and aesthetic adjuvants, such as: perfumes; pigments; dyes; optical brighteners; skin protecting and conditioning agents, e.g., lanolin, solubilized lanolins; bactericides; chemical stabilizers, e.g., sodium bisulphite; foam stabilizers, e.g., lauric myristic diethanolamide; buffering agents and pH adjusters, e.g., triethanolamine, hydrochloric acid, phosphates; bodying agents, e.g., clays; superfatting agents, e.g., stearic acid; anti-redeposition agents and soil dispersants, e.g., polyvinyl alcohol, sodium carboxymethyl cellulose; gums, e.g., sodium alginate, which also functions as a slip improving agent; and abrasive or scouring components, e.g., silic. Usually the present bars, when intended for personal use, do not and should not contain any builder salts or fillers other than those which may accompany, usually unavoidably, other components of the product. However, in certain circumstances, as when bars for heavy duty laundry use are made, it may be desirable to add builder salts, such as pentasodium tripolyphosphate, sodium carbonate and sodium silicate, and fillers, such as sodium sulphate and sodium chloride.

The proportions of the various components of the present elastic detergent bars should be kept within ranges to be given to obtain the best results and to produce a bar which will be desirably elastic, useful in place of conventional soap, soap-detergent and synthetic detergent bars and which will possess improved properties, such as described herein. In accordance with the first major aspect of the invention, as previously discussed, the synthetic organic detergent component, preferably either an anionic detergent or a mixture thereof or an amphoteric detergent or mixture thereof (with the anionic detergent-based composition also containing cross-linking agent and/or denaturant) will be from 10 to 80% of the product, preferably 15 to 50% and more preferably 20 to 25% thereof. When an anionic detergent is employed (the sole detergent) there will be present in the bar from 0.1 to 5% of a cross-linking agent and/or denaturing agent for the gelatin, preferably 1 to 3% and more preferably 1 to 2% thereof. The gelatin, preferably Type A gelatin of 225 to 300 g. Bloom, will be from 5 to 30%, preferably 7 to 25% and more preferably 10 to 20% of the finished bar or cake and the moisture content will be from 5 to 60% preferably 5 to 45% and more preferably 25 to 45%, e.g., 40%.

The lower pluralhydric alcohol, which may be omitted if syneresis problems are encountered (usually due to a high percentage of normally liquid components of the product), will normally be present in the range from 3 to 20% preferably 10 to 18%, e.g., 15%.

The total proportion of various adjuvants present, including any builders and fillers, will normally not exceed 10%, preferably will be less than 5% and more preferably will be less than 2%, with the proportion of any particular adjuvant usually being held to less than 5%, preferably less than 2% and more preferably less than 1%.

In accordance with the second aspect of this invention the synthetic organic detergent, will be from 10 to 80% of the product, preferably 35 to 65 or 70% and more preferably 35 to 55% thereof. The content of cross-linking agent and/or denaturing agent for the gelatin, when present, is usually from 0.1 to 5%, preferably 1 to 3% and more preferably 1 to 2% total. Normally the percentage of cross-linking agent will be 0.1 to 5%, preferably 1 to 2% and that of the denaturant will be 0.5 to 2%. The gelatin, preferably Type A gelatin of 225 to 300 g. Bloom, will be from 5 to 30%, preferably 7 to 25% and more preferably 10 to 20% of the finished bar or cake and the moisture content will be from 5 to 60%, preferably 10 to 40% and more preferably 10 to 30%, e.g., 25%.

As is the case with respect to the first aspect of the invention, the lower pluralhydric alcohol may be omitted if syneresis problems are encountered but if present may be utilized in the

proportions previously described with respect to such first aspect. Similarly, the proportions of various adjuvants which may be present, including any builders and fillers, will be the same.

- According to the third aspect of the invention the components with the dispersed gas (which is essentially "weightless") are preferably a mixture of anionic and amphoteric detergents, 5  
Type A gelatin of 225 to 300 g. Bloom and moisture and the proportions will be from 20 to 80% of the detergents, preferably 30 to 70% and more preferably 40 to 60%; 5 to 30% of the gelatin, preferably 7 to 25% and more preferably 10 to 20%; and from 5 to 50% of moisture, preferably 5 to 40% and more preferably 10 to 30%, all on a finished bar basis. The lower pluralhydric alcohol and mixture thereof, which may be omitted for reasons previously 10  
described, will usually be present in the range from 3 to 20%, preferably 5 to 15%, e.g., 10%.  
A lower alkylene glycol di-higher fatty acid ester anti-tack component will desirable be present and often constitutes from 0.2 to 5%, preferably 0.2 to 2%, and more preferably 0.3 to 1%, e.g., 0.5 or 0.6% of the finished bar. When a cross-linking agent and/or a denaturing agent is present the proportion thereof will usually be from 0.1 to 5%, preferably 0.7 to 2%. 15  
The proportion of fumed silica or similar bodying agent, when present, will generally be in the range from 1 to 5%, preferably 2 to 4% and the proportion of phosphate buffering agent (also possessing some building properties) will usually be from 0.5 to 4%, preferably 0.7 to 2%. The proportions of any other adjuvants present, including any builders and fillers, will be as previously described with respect to other aspects of this invention.  
In the fourth aspect of the invention the synthetic organic detergent component, preferably 20  
either anionic synthetic organic detergent or a mixture thereof with amphoteric synthetic organic detergent (proportions of nonionic and cationic detergents, if present, are considered separately, below) will be from 10 to 70%, preferably 30 to 60% of the bar. Thus, when anionic detergent such as triethanolamine polyethoxyalkyl phenol sulphonate (Cellopal 100) 25  
is employed the proportion thereof will generally be in the range from 35 to 55%, e.g., 40 to 50%. When the mixtures of anionic and amphoteric detergents are utilized the more preferred total percentage will be from 20 to 50% and the proportion of anionic detergent to amphoteric detergent will preferably be in the range from 5:1 to 1:5, more preferably 3:1 to 1:3 and still more preferably 5:2 to 2:5. When the total content of anionic and amphoteric detergents is less 30  
than 20% there will normally be sufficient nonionic detergent present to raise the total of anionic, amphoteric and nonionic detergent to at least 20% in the detergent bar. The gelatin, preferably Type A gelatin of 225 to 300 g. Bloom, will be from 8 to 35% of the bar, preferably 12 to 30% or 15 to 25% thereof. The lower pluralhydric alcohol content will be from 20 to 65% of the bar, preferably 20 to 55% or 20 to 50% thereof. Nonionic surface active agent content, including nonionic detergent content, will normally be in the range from 1 to 25% when 35  
present and may preferably be 5 to 20%. When a cross-linking agent and/or a denaturant is present the proportion thereof will usually be from 0.1 to 5%, preferably 0.7 to 2%. The proportion of fumed silica or similar bodying agent will generally be in the range from 1 to 5%, preferably 2 to 4% and the proportion of phosphate buffering agent, if present, will usually be 40  
from 0.5 to 4%, preferably 0.7 to 2%. The total of any other adjuvants present, including builders and fillers, will normally not exceed 20%, preferably being less than 5% and more preferably being less than 2%, with the proportion of any particular adjuvant usually being less than 10%, preferably less than 2% and more preferably less than 1%. Particular preferred elastic detergent bars of this aspect of the invention comprise from 20 to 60% of 45  
triethanolammonium polyethoxy alkyl phenol-sulphonate, 15 to 25% of gelatin and 20 to 55% of glycerol; 20 to 60% of triethanolammonium higher fatty alcohol sulphate, 15 to 25% of gelatin and 20 to 55% of a mixture of glycerol and propylene glycol in a ratio in the range of 5:1 to 1:2; 8 to 40% of triethanolammonium higher fatty alcohol sulphate, 5 to 30% of triethanolammonium 1-carboxymethyl-1-carboxyethoxy-ethyl-2-coco-imidazolinium 50  
betaine, 15 to 30% of gelatin and 20 to 65% of pluralhydric alcohol; 10 to 25% of triethanolammonium lauryl sulphate, 7 to 20% of triethanolammonium 1-carboxymethyl-1-carboxyethoxyethyl-2-coco-imidazolinium betaine, 15 to 25% of gelatin, 20 to 50% of glycerol, 5 to 20% of propylene glycol, 1 to 10% of nonionic surface active agent (polyoxyethylene sorbitan monolaurate or a coco monoethanolamide or mixture thereof) and 55  
from 1 to 5% of fumed silica; and 2 to 15% of myristyl triethoxy diethanolamine sulfate, 3 to 15% of triethanolammonium 1-carboxymethyl-1-carboxyethoxyethyl-2-coco-imidazolinium betaine, 10 to 20% of polyoxyethylene sorbitan monolaurate, 3 to 15% of cocodiethanolamide, 15 to 30% of gelatin and 40 to 60% of glycerol.  
Mixtures of various materials within the classification mentioned above may be employed in 60  
place of single pure materials and it is contemplated that technical chemicals, containing relatively small percentages of impurities, will be utilized, as well as those which are chemically pure. Within the percentage and proportion ranges given satisfactory elastic detergent bars are obtainable and with the present specification as a guide, one of skill in the art will be able to adjust the various percentages and proportions within the ranges given so as 65  
to produce the most satisfactory products. However, when percentages and proportions

outside the ranges and ratios recited are utilized less desirable detergent bars will result, often being excessively firm or soft, inelastic (often being malleable instead), tacky, poorly foaming, subject to excessive shrinking and syneresis or weeping or otherwise being unacceptable commercially.

5 The manufacture of the present elastic detergent bars is comparatively simple, often  
requiring only the mixing together of the components under such conditions that the gelatin  
will form a satisfactory gel with water and/or with any other solvents and other components  
present. For example, all the components of a particular detergent bar composition, including  
10 synthetic detergent, gelatin, water, cross-linking agent and/or curing agent, when present,  
and pluralhydric alcohol, when present, may be mixed together and heated, with stirring, to  
dissolve the gelatin. Alternatively, the gelatin may first be dissolved in water and the other  
components may then be admixed or other operative mixing sequences may be adopted. If the  
components are soluble the product may be transparent or at least translucent but if insoluble  
15 ingredients are employed, which may be done intentionally, an opaque gel may result. To  
clarify transparent gels and to increase the strengths and densities thereof these may be  
deaerated or degassed under vacuum or by allowing the hot or warm liquid to stand until it  
becomes clarified. Alternatively, air or other suitable gas may be distributed throughout the  
gel before solidification thereof. The solution or dispersion may then be poured into suitable  
20 moulds, chilled and thereby solidified. Gelatin dissolves at temperatures above 40 to 45°C. but  
it is normally undesirable to heat it to a temperature above 100°C. and preferably dissolving  
will take place at a temperature in the range of 50 to 90 or 95°C., more preferably 60 to 80°C.  
and over a period of from 3 to 30 minutes. Moulds will usually be at a temperature of from 5 to  
20°C., preferably 5 to 15°C. After the gelatin has completely set, which may take from about  
one minute to one hour, usually taking from three to ten minutes, the elastic detergent bar or  
25 cake may be removed from the mould and packed or may be allowed to warm to room  
temperature before packing, at which temperature it still remains firm, yet elastic.

The method described above is essentially that utilized in the manufacture of the bars of the  
first aspect of this invention. Such method may also be employed, sometimes with  
modifications, in manufacturing other elastic detergent bars of this invention. In a  
30 modification of this method, especially suitable for making the bars of the second and third  
aspects of this invention, the total proportion of water plus solvent, plasticizer and similar  
components present will be in the ranges described for water alone in the final bar without  
such other ingredients but during dissolving of the gelatin, during which time the temperature  
may be raised, enough additional water may be employed initially to facilitate solution and the  
35 mix may be heated for a period sufficient to drive off water or water plus solvent, etc. to the  
extent of from 15 to 50% of the weight of the mixture, preferably 20 to 40% thereof. In  
addition to heat, vacuum may be applied to facilitate removal of such moisture and any  
volatile solvent present, such as ethanol. Normally the additional heating to remove the  
moisture, depending on whether or not vacuum is also employed, may take from 1 to 30  
40 minutes, preferably from 1 to 15 minutes. Under this variation of the second aspect of the  
invention and similar variations of other aspects of the invention the moisture content will  
often be lower, normally being from 5 to 40%, preferably 10 to 40% and more preferably 10 to  
30%, e.g., 15%. After removal of the moisture the mix may be moulded in the manner  
previously described but the product resulting will be firmer than would be the case had the  
45 excess water not been removed. In following the method described in the immediately  
preceding sentences the various components of the bar may first be mixed together in a solvent  
medium and the gelatin may be dissolved therein or the gelatin may first be dissolved and the  
additional components added later.

The first part of the method employed in manufacturing the bars of the third aspect of the  
50 invention, those wherein air or other suitable insoluble gas is dispersed in fine bubbles  
throughout the bar, is essentially the same as that immediately previously described and it is  
also often desirable to utilize heat and vacuum to assist in dissolving the gelatin and also for  
removing excess moisture and solvent so as to make a firmer product. Additionally,  
application of the vacuum, such as one of 25 to 250 mm. Hg absolute, removes air bubbles  
55 with the moisture so that subsequent addition of very finely divided bubbles can be subject to  
better control.

After dissolving of the bar components and after optional evaporation off of some of the  
moisture content of the mix the temperature will usually be lowered to 30 to 45°C. and gas,  
preferably air, will be mixed with the gel to form finely divided bubbles therein, as previously  
60 described. Such mixing may be mechanical, as with known "Lightnin" or "Eppenbach"  
homogenizing mixers, which blend ambient air with the gel, or diffusers, injectors,  
distributors, aerators or other means may be used to incorporate gas into the gel, preferably in  
conjunction with sufficiently vigorous mixing to create enough turbulence in the mixture to  
promote blending in with it of the finely divided gas bubbles. Normally the homogeneous  
65 addition of gas bubbles will increase the volume of the mix from 5 to 60%, preferably 10 to



50%, so that the bar made will have a density lower than that of water, usually being in the range from 0.5 to 0.98 g./cc., preferably 0.65 to 0.9 g./cc., e.g., 0.8 g./cc. The gasified mixture is then poured into suitable cooled moulds which are usually at a temperature of 5 to 20°C., preferably 5 to 15°C. After the gelatin composition has completely set, which may take 5 from about one minute to an hour, usually taking from three to ten minutes, the elastic detergent bar or cake may be removed from the mould and packed or it may be allowed to be warmed to room temperature before packing, at which temperature it still remains firm, yet elastic. 5

The process for manufacturing the elastic detergent bars of the fourth aspect of this invention differs from those previously described because normally water will not be utilized 10 to dissolve the gelatin or if used, will be entirely removed during the processing. However, the initial processing is essentially the same as that employed in the other three aspects of the invention, with the substitution of lower pluralhydric alcohol for water. Thus, various mixing sequences may be employed to dissolve the gelatin in the lower pluralhydric alcohol and/or 15 any other components present, at an elevated temperature, preferably in the 80 to 100°C. range. Such dissolving will usually take from 3 to 20 minutes, after which the mix will be poured into suitable cooled moulds which are usually at a temperature of from 5 to 30°C., preferably 5 to 20°C., in which the mixture is cooled to a temperature of from 5 or 10 to 25 or 20 30°C., preferably 5 to 20°C., to completely set the composition, which may take from about one minute to an hour and usually takes from 3 to 20 minutes. If desired, the process may be varied by aerating the bar in accordance with the procedure of the third aspect of the invention, previously described. Thus, it may be cooled to an intermediate temperature, e.g., 25 30 to 60°C., after dissolving of the gelatin, and a gas, preferably air, may be mixed with the gelatin, etc. to form finely divided bubbles, utilizing the same mixing technique previously described. The volume of the mix will be increased accordingly and the final product density will be the same as that previously described for other aerated elastic detergent bars. 25

The elastic detergent bars of this invention possess an important novelty advantage over ordinary soap or detergent bars. They are especially attractive to children when they are 30 moulded to special shapes, such as the shapes of storybook, fairy tale or cartoon characters, people or animals, and promote the enjoyment of bathing by infants and young children. Because the product is elastic such moulded items seem more life-like or real to the young child. The elastic nature of the product also helps to allow a controlled dispensing of detergent and foaming materials and other utilitarian and aesthetic substances onto the skin or into the 35 bath water in response to repeated squeezings and relaxings of the bar. Thus, the utilitarian detergent is also an interesting toy. However, the product has various other advantages apart from its play value. The presence of gelatin adds a skin care ingredient to the composition and because of the bar's elasticity, breakage in shipment or during storage is minimized. Furthermore, large quantities of detergent may be present in the composition without the 40 need for extensive use of expensive waxes, special plasticizers, bodying agents, etc., to control the dissolvings of the bars and to give them desirable tactile properties and good appearances. The bars do not slough excessively, as often do ordinary detergent and soap bars and additionally they maintain substantially their original shapes during use, continually 45 dispensing detergent when rubbed onto the skin, worked in the hands or repeatedly compressed and relaxed. While the elastic detergent bars of the different aspects of this invention have particular advantages, those of the third and fourth aspects are improvements 45 over those previously described. Thus, although all the bars are useful as amusing detergent products intended primarily for use by children and are acceptable washing agents those of the third aspect possess additional high temperature stability, allowing them to be stored at temperatures higher than normally encountered without excessive softening and distortion. 50 Similarly, those of the fourth aspect are of continued good foaming properties during use (some of the other bars tend to foam less as they are repeatedly wetted and dried during normal use). Thus, such improved bars can be used for usual minimums of several hundred washings for a 100 gram bar or ten or more baths for a 150 gram bar or proportionate combinations thereof. Such improved bars are also of improved elevated temperature 55 stability and can be shipped and stored at temperatures up to 45 or 50°C. without undue deformation. 55

The following Examples illustrate but do not limit the invention. Unless otherwise indicated all temperatures are in °C. and all parts are by weight. Examples 1-7 illustrate the first aspect of the invention, Examples 8-11 illustrate the second aspect of the invention, Examples 12-14 60 show the third aspect of the invention and the fourth aspect is exemplified in Examples 15-21. 60



*Example 1*

		Percent	
	Gelatin (225 g. Bloom, Type a)	10.5	
	Glycerin	15.8	
5	Sucrose	7.9	5
	Potassium alum	1.6	
	Hydrochloric acid (50% by volume aqueous solution)	1.1	
	Deriphat 160C (30% aqueous solution of the partial sodium salt of	63.1	
10	N-lauryl betainodipropionate, mfd. by General Mills, Inc.)		10

The components of the above formula are blended together and are heated with stirring at a temperature in the range 60 to 80°C. to dissolve the gelatin and the various other materials. After 5 to 10 minutes a clear solution or gel is obtained, which is poured into shaped moulds and chilled to 15°C. After solidification, which takes about 8 minutes, the elastic detergent bar or cake is removed from the mould and is ready for use.

The product is satisfactorily elastic and cleans well, when employed as a bath or hand "soap", although the foaming effects thereof are not as good as when preferred anionic detergents are employed instead of the amphoteric detergent component. However, the bar is a useful washing product and maintains its elasticity throughout repeated washings and dryings.

When the formula is modified so that the weights of all components except the Deriphat 160C are maintained the same and the amount of Deriphat 160C is increased to 68.4% essentially the same type of elastic detergent bar results. Also, when the alum is replaced by urea good elastic detergent bars of essentially the same properties are produced. However, with neither the alum cross-linking agent nor the urea denaturant present products of the described formulation are somewhat more flexible and softer to the touch and may tend to develop more syneresis.

When the formula is modified to replace the sucrose with propylene glycol a useful product of comparable properties is obtained, which is also the situation when the total percentage of glycerol and other dihydric polyhydric compound present (propylene glycol and/or sucrose and/or dextrose) is reduced to 5 to 10%. Reduction of the pluralhydric alcohol content usually results in firmer or harder gels which are especially satisfactory for the present detergent bars. When the proportion of Deriphat 160C is reduced to 30, 40 and 50% of the product (9, 12 and 15% active ingredient) diminutions in foaming power result but the bar becomes firmer. A similar firming effect is obtained when 300 g. Bloom gelatin is employed instead of that of 225 g. Bloom or when more gelatin is employed. Of course, formula modifications will be made, with the guidance of this disclosure, to produce the best products for particular applications. In making all the variations of the formula mentioned above the processes employed are the same.

In a modification of such processes, desirably followed, the hot mixture is allowed to stand at an elevated temperature in the range from 45 to 60°C. for a period of one hour so as to allow all air bubbles therein to be dissolved or to rise to the top of the mix and separate therefrom, before setting of the gel. The products resulting are brighter and clearer in appearance following such deaeration. Alternatively vacuum may be used, in supplementation of or in replacement of part of the described method.

In further modifications of the procedure small proportions, e.g., 0.01 to 0.5%, of dyes and pigments are incorporated to colour and opacify the products and the gels are moulded in chilled moulds into the shapes of storybook characters, cartoon characters and animals, such as green frogs, yellow ducks, brown dogs and orange cats, with the proportions of the dyes and pigments being about 0.02% for dyes and about 0.2% for pigments. The dyed bars are transparent or translucent and the pigmented bars are opaque. The opacities of the pigmented bars are further increased by additions of 1, 2 and 5% of powdered clay to the mix, which also converts the colours to pastels.

*Example 2*

		Percent	
	Gelatin (225 g. Bloom, Type A)	10.0	
	Glycerin	15.0	
5	Sucrose	7.5	
	Potassium alum	1.5	
	Triethanolammonium lauryl sulphate	12.5	
	Ethanol	3.6	
	Lauric myristic diethanolamide	3.3	
10	Methyl cellulose	0.5	1
	Formaldehyde	0.1	
	Perfume	0.2	
	Other adjuvants and impurities (sodium chloride, dyes, fluorescent brighteners, triethanolamine, citric acid)	3.0	
15	Water	42.8	1

Elastic detergent bars, each 100 g. in weight, are made by the method described in Example 1 (much of the ethanol is evaporated off) and the products resulting are firmly elastic, satisfactory, high foaming detergent bars which emit foam readily upon squeezing. The bars are transparent and light in colour but may be made coloured and/or opaque by addition of dyes, pigments and insoluble fillers or bodying agents, such as powdered clays, in accordance with Example 1. The detergent bars maintain their good foaming properties during repeated uses and yield up to 200 to 300 normal hand washing uses and up to 10 bath uses per bar. They are mild to the hands and skin (the gelatin content helps), do not slough objectionably, do not excessively bleed or exhibit syneresis and can withstand normal use at ordinary room and wash water temperatures, e.g., 25°-40°C., without loss of shape. When the alum cross-linking agent is replaced by other such cross-linking agents, e.g., equivalent proportions of aluminium chloride, zinc sulphate, magnesium sulphate and/or calcium chloride or by urea or equivalent denaturant similarly firm elastic bar products result. However, when the cross-linking agent and denaturant are omitted from the formula the product is noticeably softer and may be less desirable for some commercial uses. Instead of the triethanolammonium lauryl sulphate, diethanolammonium cetyl sulphate may be satisfactorily substituted but when sodium lauryl sulphate is utilized the product resulting is much cloudier in appearance although it is still an elastic gel-type bar. However, when ammonium cocomonoglyceride sulphate or a mixture of equal parts thereof with the corresponding sodium salt is substituted for the triethanolammonium lauryl sulphate good elastic detergent bars are produced.

When the proportions of the various components are varied  $\pm 10\%$ ,  $\pm 20\%$ ,  $\pm 30\%$ , e.g., by increasing the glycerol content from 15% to 16.5%, 18% and 19.5%, while maintaining the other proportions within the limits given in the specification, similar useful elastic detergent bars result.

*Example 3*

		Percent	
45	Gelatin (225 g. Bloom Type A).	10.0	4
	Glycerol	5.0	
	Dextrose	5.0	
	Urea	1.0	
	Triethanolammonium lauryl sulphate	15.0	
50	Ethanol	4.3	
	Lauric myristic diethanolamide	4.0	
	Methyl cellulose	0.6	
	Formaldehyde	0.1	
	Perfume	0.2	
55	Other adjuvants and impurities (sodium chloride, dyes, fluorescent brighteners, triethanolamine, citric acid)	3.6	
	Water	51.2	

When the above formula is made by the method of Example 1 good elastic detergent bars of the previously described desired properties are obtained.

*Example 4*

The experiments of Example 1 are repeated, with Miranol C<sub>2</sub>M, anhydrous acid, and triethanolamine (forming the triethanolammonium salt) being substituted for the Deriphat 160C active ingredient, cross-linking agent, acidifying agent (HCl) and sucrose and with 300 g. Bloom gelatin being substituted for the 225 g. Bloom gelatin. Thus, the mentioned

components, totalling 28% of the Example 1 formulation, are replaced with 21% of Miranol C<sub>2</sub>M and 7% of triethanolamine. The detergent bar made is elastic, form-retaining at normal use temperatures and of satisfactory cleaning power. The triethanolamine also acts as a buffer.

#### Example 5

	Percent	
Triethanolammonium lauryl sulphate	18.0	
Glycerol	9.0	
10 Gelatin (225 g. Bloom, Type A)	9.0	10
Potassium alum	1.0	
Sodium carboxymethyl cellulose	0.1	
Polyvinyl pyrrolidone	0.1	
Carbowax 600 (polyethylene glycol)	4.0	
15 (CARBOWAX is a Trade Mark)		15
Water	58.8	

#### Example 6

	Percent	
20 Triethanolammonium lauryl sulphate	18.0	20
Glycerol	5.0	
Gelatin (225 g. Bloom, Type A)	9.0	
Potassium alum	1.0	
Sodium carboxymethyl cellulose	0.1	
25 Polycinyl pyrrolidone	0.1	25
Carbowax 600	8.0	
Water	58.8	

#### Example 7

	Percent	
30 Triethanolammonium lauryl sulphate	18.0	30
Gelatin (225 g. Bloom, Type A)	9.0	
Potash alum	1.0	
Polyvinyl pyrrolidone	0.5	
35 Carbowax 600	10.0	35
Water	61.5	

The moulded elastic detergent bar products of Examples 5-7, made by the method of Example 1, are good deterative bar products, satisfactory for bath use and hand washing. They are of stable form, continue to be elastic during use and foam well. Although these bars may have a slight tackiness on the surface thereof, as do some of the other products of this invention, such may be corrected by dusting with talc, starch or other similar agent. Similar bars result with Type B gelatin.

#### Example 8

	Percent	
Triethanolammonium lauryl sulphate	8.0	
Gelatin (300 g. Bloom, Type A)	10.0	
Propylene glycol	10.0	
50 Triethanolamine salt of Miranol C <sub>2</sub> M anhydrous acid	28.0	50
(triethanolamine 1-carboxymethyl-1-carboxy-ethoxyethyl-2-coco-imidazolinium betaine)		
Water	44.0	

The components of the above formula are blended together and are heated, with stirring, to a temperature in the range from 60 to 80°C. to dissolve the gelatin and the various other materials. After about 5 to 10 minutes a clear solution or gel is obtained, which is poured into shaped moulds and chilled to 15°C. Upon solidification, which takes about eight minutes, the elastic detergent bar or cake is removed from the mould and is ready for use. The product is satisfactorily elastic and cleans well when it is employed as a bath or hand "soap". It foams very well on initial use and although the foam is diminished upon subsequent uses the bar is a useful washing product and maintains its elasticity throughout repeated washings and dryings. Such bar, containing amphoteric and anionic synthetic organic detergents with gelatin, does not slough objectionably during use and is less tacky and better foaming than previous bars based on only anionic or amphoteric detergents, respectively.

In a modification of the manufacturing process the hot mixture of bar components is allowed to stand at an elevated temperature in the range of 45 to 55°C. for a period of one hour so as to allow all air bubbles therein to be dissolved or to rise to the top of the mix and separate therefrom before setting of the gel. The products resulting are brighter and clearer in appearance following such deaeration, during which relatively little water and other solvents are evaporated. However, when the temperature of the mixture is raised, e.g., to 60 or 65 to 80 or 90°C., as it is in other embodiments of this example, appreciable loss of water and other volatile materials results and the moisture content of the resulting bar is appreciably diminished. Thus, utilizing a 15 to 30 minute heating period at 80°C., especially in the presence of vacuum, e.g., 250 mm. Hg absolute pressure, from 20 to 40%, e.g., 25%, of the mix weight is removed. After the evaporation off of 25% of the mix the elastic detergent bar produced includes 11% of triethanolammonium lauryl sulphate, 13% of gelatin, 13% of propylene glycol, 38% of Miranol C<sub>2</sub>M, as the triethanolammonium salt, and 25% of water. The elastic detergent bars resulting (deaeration may be effected, too) are firmer, tougher and less liable to shrink upon prolonged exposure to the atmosphere during storage.

When the formula is modified to replace the triethanolammonium lauryl sulphate with the same weight of other suitable anionic detergent, such as ammonium cocomonoglyceride sulphate or a mixture of equal parts of ammonium cocomonoglyceride sulphate and sodium cocomonoglyceride sulphate and when the propylene glycol is replaced by glycerol a product of comparable properties results. Similarly, when the Miranol C<sub>2</sub>M salt is replaced by Deriphat 151 or Deriphat 160 or other suitable amphoteric detergent, especially one of the imidazolinium betaine, betaaminopropionate or betaaminodipropionate type and when the gelatin is replaced by 15% of 225 g. Bloom Type A gelatin (Type B may also be used but is not usually as good) essentially the same type of elastic detergent bar results. Similarly, when 2% of potash alum (cross-linking agent) or 1% of urea (denaturant) is present in replacement of a corresponding percentage of water a firmer bar results. When adjuvants are employed, such as fluorescent brighteners; bactericides; emollients; solvents; foaming agents, e.g. lauric myristic diethanolamide; pH adjusting agents, e.g., hydrochloric acid, triethanolamine; perfumes; colorants, including dyes and pigments; and preservatives, they contribute their specific properties to the final bar.

In further modifications of the formula small proportions of dyes and pigments are incorporated to colour and opacify the products and gels are moulded in chilled moulds into the shapes of specific storybook, nursery rhyme, cartoon and animal characters, with the proportions of dyes and pigments employed being about 0.02% for the dyes and about 0.2% for the pigments. The dyed bars are transparent or translucent and the pigmented bars are opaque. The opacities of the pigmented bars are further increased by additions of 1, 2 and 5% of powdered clay to the initial mixture, which also converts the colours to pastels.

The formulas described in this example are modified proportionately  $\pm 10\%$ ,  $\pm 20\%$  and  $\pm 30\%$ , within the ranges given and the products resulting are useful elastic detergent bars of this invention.

#### Example 9

	Percent	
Ammonium cocomonoglyceride sulphate (47% active ingredient)	24.2	4'
Triethanolamine salt of Miranol C <sub>2</sub> M	28.0	
Gelatin (300 g. Bloom. Type A)	10.0	
Propylene glycol	10.0	
Water	27.8	5'

Elastic detergent bars of the above formula and of such a formula less 25% of water, removed in a drying operation after dissolving of the gelatin, are made according to the method of Example 8. The bars produced are useful elastic detergent bars for bath use or handwashing and are less tacky and better foaming than similar bars not containing the mixture of anionic and amphoteric detergents. Also, the bars made by a process including removal of moisture, as described, are less liable to shrink on storage, exposed to the air, than are similar bars containing greater percentages of moisture. The improved bars, made by reducing the moisture content, analyze about 30% of ammonium cocomonoglyceride sulphate, 35% of triethanolammonium 1-carboxymethyl-1-carboxyethoxyethyl-2-cocimidazolinium betaine, 13% of gelatin, 12% of propylene glycol and 10% of water. The removal of moisture in the above-described process and other such processes of this invention takes place at a temperature of 30 to 90°C., preferably 40 to 80°C., the lower temperatures being used most when vacuum is also employed.

*Example 10*

		Percent	
	Miranol C <sub>2</sub> M, anhydrous acid	21.0	
	Triethanolamine	7.5	
5	Propylene glycol	10.0	5
	Gelatin (300 g. Bloom, Type A)	10.0	
	Triethanolamine lauryl sulphate	28.5	
	(40% active ingredient, aqueous solution)		
10	Ammonium cocomonoglyceride sulphate	23.0	10
	(47% active ingredient, aqueous solution)		

Following the procedure of Example 8, products of the above formula are made, without moisture removal. They are good elastic detergent bars for both bath use and handwashing and are less tacky and better foaming than similar bars containing either anionic detergent or amphoteric detergent alone. Also, because of their comparatively low moisture content the bars are less liable to shrinkage on storage and when exposed to air than are similar bars containing more moisture.

In normal handwashing use a 100 gram moulded bar and moulded items in the shapes of cartoon characters, automobiles and animals last for at least 200 handwashings at a water temperature of 40°C., give a copious foam and wash well. Additionally, they leave the hands feeling soft, apparently due to the gelatin and amphoteric detergent contents of the products. When 150 gram bars or articles are utilized they last for as many as 20 normal baths, with good foaming throughout such use. During wearing down of the 'bars' they substantially retain their general original shapes, colours and foaming and washing abilities.

*Example 11*

The product of Example 10 is made from an initial mixture which includes 45% of water instead of the 30% in the final product and in the mix of Example 10. The excess moisture is removed during manufacturing by heating for about 45 minutes at a temperature of about 75°C., without vacuum. Comparison of the products of Examples 10 and 11 shows little difference between them except that the product of Example 11 may have the components thereof more uniformly distributed throughout it due to the initial dissolvings of more of them in the aqueous medium before removal of excess moisture. Also, initial mixing and dissolving of the mix of this example is much easier. In a further modification of this example the density of the product is diminished 10%, so that it will float in warm bath water, by distributing small bubbles of air throughout it after removal of excess moisture from the mixed solution and after cooling of such mix, following the procedure of the third aspect of this invention, described in following Examples 12-14. The product resulting is an excellent 'floating soap' for use in the bathtub, leaves no ring and is a superior floating toy for children which helps them to enjoy taking baths.

*Example 12*

		Percent	
	1-Carboxymethyl-1-carboxyethoxyethyl-2-coco	21.0	
	iminodazolium betaine		
45	Triethanolamine	7.5	45
	Propylene glycol	10.0	
	Triethanolammonium lauryl sulphate (40% active	47.0	
	ingredient aqueous solution)		
50	Fumed silica (Cab-O-Sil M-5; CAB-O-SIL	3.0	50
	is a trade mark)		
	Gelatin (300 g. Bloom, Type A)	10.0	
	Ethylene glycol distearate	0.5	
	Monosodium phosphate	0.3	
55	Disodium phosphate	0.7	55

The components of the above formula are mixed together in a mixing tank equipped with a 'Lightnin' homogenizing mixer and the speed of the mixer is adjusted to be slow enough so as not to entrain objectionable proportions of air in the mix. The temperature is raised to about 75°C. and mixing is effected for about 15 minutes, during which time the gelatin and other soluble materials dissolve and a homogeneous mixture is produced. During that period the triethanolamine reacts with the Miranol C<sub>2</sub>M to form the corresponding triethanolamine salt thereof or its ionized equivalent. After production of the homogeneous mixture the temperature thereof is lowered (heating and cooling coils are present in the mixing tank) to about 40°C., at which temperature the homogenizing mixer speed is increased sufficiently to entrain air in the mix. Mixing is continued for an additional five minutes, during which time

the volume of the mix in the mixer increases about 30%, so as to fill the mixer to within 10% of its volume. The mix is then poured into cooled moulds which are at a temperature of 10°C. and in them it is lowered to a temperature of about 15°C., at which it is solidified, with the air bubbles entrapped therein. Such bubbles are principally of diameters in the range of one micron to one mm. and the density of the moulded elastic detergent bar produced is about 0.8 g/cc. The bar moisture content is about 28.5%.

The product made is a useful elastic detergent bar of acceptable surface characteristics (smooth and non-tacky), good detergency and improved elevated temperature storage characteristics. It floats in water (having a density of about 0.8 g./cc.) and during use does not slough objectionably. When wrapped and stored in cases at a temperature of 43.5°C. for a month no distortion of the moulded bar due to softening or melting results. The combination of elasticity and porosity due to the moulded-in air content, homogeneously distributed throughout the bar in the form of minute bubbles, aids in developing foam from the bar when it is repeatedly compressed and released and/or rubbed against the skin. Also, the bar resists breakage during storage, transportation and use and substantially retains its original moulded form during use.

When modifications are made in the manufacturing procedure in accordance with the previous description similarly satisfactory bar products result. Thus, when instead of a Lightnin mixer, an Eppenbach homogenizing mixer is used, a substantially identical product results. When the amphoteric betaine detergent is charged as its triethanolamine salt and any excess triethanolamine of the formula is charged as such the bars produced are also satisfactory. Elimination of the phosphates, ethylene glycol distearate, fumed silica and even of the propylene glycol from the formula still results in the production of a useful elastic detergent bar, which is also made by the same method when only the amphoteric detergent, gelatin and a suitable medium for gelation are present, together with the entrapped gas bubbles. Replacing the amphoteric betaine with other amphoteric detergents, such as those previously described herein, e.g. Deriphat 151, Deriphat 160 and 50:50 mixtures thereof, also results in satisfactory products, as does replacement of the triethanolamine (or triethanolammonium) lauryl sulphate with ammonium cocomonoglyceride sulphate and others of the anionic detergents mentioned in the specification. Instead of the 10% of 300 g. Bloom Type A gelatin there may be employed 14% of 225 g. Bloom Type A or similar quantities of corresponding Type B gelatins and useful products result, although the Type A and higher Bloom rating gelatins make more stable and firmer products. Of course, when potash alum or urea or other cross-linking or denaturing agents are present to the extent of 1.5 and 1% respectively, or in mixture, in replacement of some of the water in the formulation, firmer bar products result. Replacement of the dispersed air with other insoluble gases, such as argon, nitrogen and carbon dioxide, also produces useful products but because of the solubility of the carbon dioxide in water, especially during use of the bar, it is less preferred. Spargers or other bubble generators may be employed to disperse the gases into the mixtures.

In another variation of the process described, after the mixing together of the bar components in the Lightnin homogenizing mixer and before cooling of the mix and the blending of gas with it, the mix is heated so as to maintain it at a temperature of 70°C. for an additional ten minutes at a vacuum of 200 mm. Hg absolute to evaporate off enough moisture, about 10% of the weight of the mix, so as to make the final bar moisture about 20.6%. A firmer bar results, which shrinks less on storage.

Further variations are made in the formula of Example 12 by varying the proportions of the described components  $\pm 10\%$  and  $\pm 25\%$ , while still keeping them within the ranges previously given in the specification. Useful elastic detergent bar products of the qualities previously mentioned result.

#### Example 13

	Percent	
Miranol C <sub>2</sub> M (anhydrous acid)	21.0	
Triethanolamine	7.5	
Propylene glycol	10.0	
Triethanolammonium lauryl sulphate (40% active ingredient aqueous solution)	23.5	
Cab-O-Sil M-5	3.0	
Gelatin (300 g. Bloom, Type A)	10.0	
Ethylene glycol distearate	0.5	
Monosodium phosphate	0.3	
Disodium phosphate	0.7	
Ammonium cocomonoglyceride sulphate (47% active ingredient aqueous solution)	23.5	

The above formula is mixed together and the components thereof are processed by the method described in Example 12, without evaporation of moisture. When poured into moulds and solidified the elastic detergent bars resulting are of the same general desirable properties mentioned for the products of Example 12. Similarly, when the moisture content of the final bar, about 27%, is decreased to 18.9% by evaporation of about 10% of the weight of the mix before distributing air bubbles throughout it, as described in Example 12, the product resulting is firmer and has the other useful properties of such lower moisture content bars.

When the proportions of components are varied in the same manner as described in Example 12 but are kept within the ranges specified, useful and satisfactory elastic detergent bars are produced. Also, when half of the Miranol C<sub>2</sub>M is replaced with Deriphat 160 (it may be incorporated in the formula as an aqueous solution, Deriphat 160-C, but added moisture will be removed by evaporation during mixing) a product of essentially the same characteristics as that of the formula of this example is made. This is also the result when glycerol or a mixture of glycerol and propylene glycol (1:1) is employed in replacement of the propylene glycol.

In addition to the basic formulas shown in the previous examples there may be present small proportions of various common adjuvants, such as 0.5% of perfume, 0.5% of sodium alginate and/or sodium carboxymethyl cellulose, 0.1% of dye, 0.3% of pigment, 1% of stearic acid, as an emollient and 0.5% of a suitable germicide, to contribute their particular properties to the bar. Usually such materials will replace portions of the moisture content of the formulation.

#### Example 14

	Percent
Triethanolamine salt of Miranol C <sub>2</sub> M,	28.0
anhydrous acid	
Triethanolamone	0.5
Triethanolammonium lauryl sulphate (40% active ingredient, aqueous solution)	55.0
Pyrogenic silica (Cab-O-Sil M-5)	3.0
Gelatin (225 g. Bloom, Type A)	10.0
Ethylene glycol distearate	0.5
Monosodium phosphate	0.3
Disodium phosphate	0.7
Deionized water	2.0

The components of the above formula are mixed together and further processed in a manner like that described in Example 12, without evaporation of moisture. When poured into moulds and solidified the elastic detergent articles resulting are of the same general desirable properties mentioned for the products of Example 12 but are slightly softer, due to the use of the 225 g. Bloom gelatin. When the moisture content of the final bar is decreased to about 20% by evaporation of water during the manufacturing process, in the manner described in Example 12, the product resulting is firmer and has the other previously described useful properties of such lower moisture content bars. Such firmer products are also made by including 1.5% of alum and 1% of urea in the formulation in replacement of the 2% of water and 0.5% of the pyrogenic silica. When 225 g. Bloom Type B gelatin is substituted for the 225 g. Bloom Type A gelatin of this example a useful elastic detergent bar of improved elevated temperature stability also results, which is also the case when 300 g. Bloom Type B gelatin is employed. However, because the pH of the wash water from the present products is on the alkaline side, being about 9, a more stable bar is obtained when the Type A gelatin is used.

In further variations of the above experiments Miranol S<sub>2</sub>M and SHD Conc. are substituted for the triethanolamine salt of Miranol C<sub>2</sub>M and acceptable elastic detergent bars of improved elevated temperature stability are also obtained, which is also the case when instead of the Miranols various Deriphats, such as Deriphats 151, 151-C, 154, 160, 160-C and 170-C are employed, preferably in about 50:50 mixtures with such a Miranol salt. Good products result when the ratio of anionic detergent content to amphoteric detergent content is within the range from 2:1 to 1:3. This is also true when others of the anionic detergents previously mentioned are substituted for the anionic detergents of the examples. The products resulting all have densities within the 0.5 to 0.98 range and such densities are controlled, in separate experiments, by beating or sparging in more or less air so as to be 0.6, 0.7, 0.8 and 0.9. Normally, for good dissolving powers and reasonable firmness of the bar the density will be held at about 0.8 or 0.9 g./cc.



*Example 15*

	Gelatin (300 g. Bloom, Type A)	Percent	
	1-Carboxymethyl-1-carboxyethoxyethyl-2-coco-	20.0	
5	imidazolinium betaine (Miranol C <sub>2</sub> M, anhydrous acid, mfd. by Miranol Chemical Company)	8.4	5
	Triethanolamine	3.0	
	Glycerol	40.1	
10	Triethanolammonium lauryl sulphate solution (65% TEALS in propylene glycol, sold as Maprofix TLS-65 by Onyx Chemical Co.)	20.0	10
	Polyoxyethylene sorbitan monolaurate (20 mols of ethylene oxide per mol, sold as Tween 20 by Atlas Chemical Industries—TWEEN is a Trade Mark)	5.0	
15	Cab-O-Sil M-5 (fumed silica, manufactured by Cabot Corp.)	3.0	15
	Perfume	0.5	
20	A Lightnin mixer is employed to stir all the above components except the fumed silica and perfume at a constant high speed at a temperature of about 85°C. until all of the gelatin has been dissolved, which takes about 25 minutes. The fumed silica is then dispersed in the mix and finally, after cooling to a temperature below 60°C. the perfume is mixed in and the composition is poured into moulds, which have been pre-cooled to a temperature of 10°C. In them its temperature is lowered to about 15°C., at which it is completely solidified into bar forms. After solidification the elastic detergent bars are withdrawn from the moulds and are packed and stored, ready for shipment.		
25	Samples of the bars produced are tested and are found to be good foaming detergent bars, elastic in nature and capable of repeatedly foaming during normal repeated handwashings and bath uses despite being wetted and dried out many times. Additionally, the bars are of an improved elevated temperature stability, compared to other gelatin-detergent bars, being sufficiently stable at a temperature of 51°C. to maintain their shapes during storage before use, during which storage the bars are subjected to such temperature. Furthermore, the bars made are of attractive elastic condition, returning readily to initial shape after elastic deformation in the squeezing test previously described, and are good detergents. They are not objectionably tacky on the surfaces thereof nor are they objectionably hard or soft. The bars essentially retain their original moulded forms during use, and probably at least in part because of their elasticity, resist breakage during shipments.		
30	In a modification of the described formula the proportion of Miranol C <sub>2</sub> M is increased to 11.2%, the proportion of triethanolamine (to form the salt of the Miranol imidazolinium betaine) is increased to 4.0%, the percentage of glycerol is reduced to 29.0% and that of the triethanolammonium lauryl sulphate solution is increased to 33.3%. Also, the Tween 20 is replaced by 2% of cocomonoeethanolamide and the fumed silica is omitted from the formula. The manufacturing method is the same as previously described, with the cocomonoeethanolamide being included in the original mixture and with the perfume being added after preliminary cooling. The bars resulting are higher in detergent content and are better foaming and deterative products but otherwise are of similar properties to those previously described in this example.		
35	In the above modified formula the percentage of cocomonoeethanolamide may be increased to 5%, with the additional 3% replacing glycerol, and an even better foaming bar is obtained. Similarly, replacements may be with lauric myristic diethanolamide and other such higher fatty acid (C <sub>8</sub> -C <sub>20</sub> ) lower (C <sub>1-3</sub> ) mono- or dialkanolamides. Such compounds are often considered to be foam stabilizers or foam enhancers but also have deterative properties and in this specification are considered to be within the description of nonionic detergents given previously, as are amine oxides of the usual types.		
40	In variations of the above formulations and manufacturing methods, after mixing the various components, except perfumes, the temperature of the mix is lowered to 60°C., at which temperature the perfume is blended in and air is intentionally beaten into the mixture over a period of five minutes, so as to increase the mix volume about 50%, after which the mix is poured into moulds, as previously described. The product resulting, when cooled, is usually of a density of from 0.7 to 0.8 g./cc. The bar properties are similar to those for the unaerated bars previously described except that elevated temperature stability is further improved and, of course, the bars float in water. In another modification of the manufacturing method, to avoid the presence of any bubbles in the final product the mix is allowed to remain quiescent for about ten minutes at 60 to 70°C. after perfume addition and before moulding to permit any		
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dispersed air or gas bubbles to rise within it and be 'vented' to the atmosphere.

The various bars described above all have moisture contents less than 1% and several of them have less than 0.1% of moisture therein. They all conform well to body surfaces and feel especially good against the skin and leave it feeling soft.

5

#### Example 16

	Percent	
Gelatin (300 g. Bloom, Type A)	20.0	
Glycerol (dental grade)	29.5	
10 Cellopal 100 (polyethoxy [11 mols per mol] dodecyl phenol sulphonate, triethanolamine salt, sold by Tanatex Chemical Corp.)	50.0	10
Perfume	0.5	

15 The glycerol is heated to 88°C. and the gelatin powder is sprinkled into it, with stirring until the gelatin is dissolved, which takes about 50 minutes. Then the Cellopal 100 is mixed in over a period of about 12 minutes, after which the perfume is added, with the temperature at about 65°C., and the product is moulded, as described in Example 15.

20 The elastic detergent bars produced are readily removed from the moulds and are good foaming bars throughout repeated uses with intermediate dryings. They are not objectionably tacky on the surfaces thereof, are of improved and acceptable elevated temperature stability, are satisfactorily elastic, being neither too hard nor too soft and, when moulded in particular forms, such as cartoon characters, maintain such shapes for substantial proportions of their useful lives, despite repeated uses.

25 In a modification of this example when the proportion of Cellopal 100 is decreased to 40% and that of glycerol is increased to 39.5% the bar is somewhat softer and the foaming action is not as great, although the product is acceptable in both respects. Otherwise, it is similar to that described earlier in this example.

#### 30 Example 17

	Percent	
Gelatin (300 g. Bloom, Type A)	20.0	
Glycerol	28.5	
35 Maprofix TLS-65 (65% triethanolamine lauryl sulphate in 35% of propylene glycol, sold by Onyx Chemical Company)	33.3	35
Sodium bisulphite	0.5	
Cocomonoethanolamide	2.0	
Miranol C <sub>2</sub> M, triethanolamine salt	15.2	
40 Perfume	0.5	40

45 The sodium bisulphite and gelatin are dissolved in the glycerol and Maprofix mixture by heating at a temperature of 88°C. for about 45 minutes, after which a mixture of the cocomonoethanolamide and Miranol C<sub>2</sub>M, triethanolamine salt, is added and mixed in over a period of ten minutes and the perfume is mixed in over one minute. The bisulphite is utilized to stabilize the colour of the product. The composition is moulded by the method described in previous examples 15 and 16. The products made have the properties previously described for those of such examples and when gasified by the methods previously described produce similar low density bars. When the formula is modified by increasing the glycerol content to 29.5%, adding 1.5% of triethanolamine stearate (reacting stearic acid with triethanolamine) and omitting the sodium bisulphite and the cocomonoethanolamide, satisfactory elastic detergent bars are made. In the manufacturing method employed the glycerol is heated to 83°C., the stearic acid is dissolved in it with stirring over a period of about five minutes, the triethanolamine, Maprofix TLS-65 and Miranol C<sub>2</sub>M, triethanolamine salt (as Miranol C<sub>2</sub>M and triethanolamine) are dissolved in the glycerol-stearic acid melt over a period of about five minutes and the gelatin is dissolved in the resulting mixture over a period of about 50 minutes, after which perfume is added in about one minute. The composition made is moulded according to the methods previously described and the product obtained has good characteristics, like the elastic detergent bars of previous examples. It is easy to pour into moulds, easy to remove from them, of good elevated temperature stability, of good repeated foaming properties, satisfactorily elastic, non-tacky and of desirable hardness and stability.

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*Example 18*

		Percent	
	Coco fatty acid mixture (average molecular weight of 218)	22.5	
	Stearic acid (molecular weight of 268)	7.9	
5	Triethanolamine	16.7	
	Glycerol	26.9	
	Maprofix TLS-65 (dehydrated)	5.0	
	Sodium bisulphate	0.5	
	Gelatin (300 g. Bloom, Type A)	20.0	
10	Perfume	0.5	1

The coco fatty acid and stearic acid, in mixture, are heated to a temperature of 82°C. for five minutes and then the triethanolamine is added to form the corresponding soaps. After mixing for another five minutes the glycerol and the Maprofix TLS-65 are added and after an additional five minutes mixing the sodium bisulphite and gelatin are added over a period of fifteen minutes, after which the mix is maintained at 82°C. for an additional 30 minutes. Finally, after cooling to about 65°C. the perfume is added and stirred in for one minute. The mix does not aerate and does not require any deaeration. It is easy to pour and the moulded bars, made as described in the foregoing examples, are easy to remove from the moulds. The bars made are good foaming bars and repeatedly foam during use, exhibit improved elevated temperature stability, are not objectionably tacky on the surfaces thereof, are of desirable hardness (not unduly hard or soft), are satisfactorily elastic and are good detergents.

*Example 19*

		Percent	
25	Glycerol	58.8	2
	Miranol C2M, triethanolamine salt	15.2	
	Tween 20	5.0	
	Gelatin (300 g. Bloom, Type A)	20.0	
30	Sodium bisulphite	0.5	
	Perfume	0.5	3

A mixture of glycerol, Miranol C2M, TEA salt and Tween 20 is heated to 90°C. with moderate stirring and after about five minutes to it are added the sodium bisulphite and gelatin over a period of about fifteen minutes, after which the mixer speed is increased and heating and stirring are continued for an additional half hour. The mix is cooled to 70°C. and perfume is added, with stirring, over a period of about 1-1/2 minutes. The mix is moulded as in previous Examples 15-18 and the product is a satisfactory elastic detergent bar of good elevated temperature stability and good foaming and re-foaming powers.

*Example 20*

		Percent	
	Glycerol (dental grade)	48.4	
	Standapol Conc. 7023 (equal proportions of cocodiethanolamide and diethanolamine myristyl triethoxy sulphate, anhydrous, made by Henkel et Cie.)	8.0	
45	Tween 20	15.0	
	Miranol C2M, triethanolamine salt	7.6	
	Sodium bisulphite	0.5	
50	Gelatin (300 g. Bloom, Type A)	20.0	
	Perfume	0.5	

The glycerol, Standapol, Tween, Miranol and TEA (stoichiometric amount to neutralize 5.6% of Miranol C2M, anhydrous) are mixed together and heated to a temperature of 90°C., after which the sodium bisulphite and gelatin are admixed over a period of 15 minutes, with the stirring being conducted at moderate speed. Subsequently, the stirring speed is increased and mixing is continued for 1/2 hour to dissolve the gelatin. Then the mix is cooled to 75°C., and perfume is added over a period of 1.5 minutes, with stirring. The composition is then poured into moulds, as previously described. The product is an excellent elastic detergent bar of good foaming and re-foaming power, is of improved elevated temperature stability, is easy to remove from the moulds and is non-tacky.

*Example 21*

		Percent	
	Glycerol	38.8	
	Standapol Conc. 7023	25.0	
5	Miranol C <sub>2</sub> , triethanolamine salt	15.2	5
	Sodium bisulphite	0.5	
	Gelatin (300 g. Bloom, Type A)	20.0	
	Perfume	0.5	

10 The procedure of Example 20 is repeated with the glycerol, Standapol and Miranol being first admixed and heated, the sodium bisulphite and gelatin being added and dissolved and the perfume being added to the partially cooled mix, followed by moulding. The product is a satisfactory elastic detergent bar of good foaming and re-foaming characteristics, of improved elevated temperature stability and of satisfactory tactile properties and appearance.

15 When in the preceding examples the 300 g. Bloom Type A gelatin is replaced with 1.2 times as much of 225 g. Bloom Type A gelatin or with a corresponding quantity of Type B gelatin of the same Bloom value, useful elastic detergent bars result although Type A gelatins are preferred to produce the best bars. Also, when instead of the Miranol C<sub>2</sub>M salt there are substituted in the preceding formulations other lower alkanolamine salts, e.g. diethanolammonium salts, and Deriphats 151 and 160, similar useful products result. This is also the case when triethanolamine lauryl sulphate, triethanolamine stearate, triethanolamine cocate-stearate, Cellopal 100, the alkyl sulphate of Maprofix TLS-65, Tween 20, cocomonoeethanolamide, cocodiethanolamide and Standapol Conc. 7023 are replaced by others of the named anionic detergents and nonionic detergents, respectively. Furthermore, 25 replacements with the other mentioned detergents of the same anionic, nonionic or amphoteric types result in similarly acceptable products of desirable characteristics when the formulations made are produced with the guidance of the present specification. Likewise, variations in the proportions of the various components of  $\pm 10\%$ ,  $\pm 20\%$  and  $\pm 25\%$  of the amounts given in Examples 15-21 produce acceptable and satisfactory elastic detergent bars of 30 desirable characteristics when such varied proportions are within the ranges specified herein.

**WHAT WE CLAIM IS:-**

1. An elastic detergent bar comprising synthetic organic detergent, gelatin and a liquid medium which is water and/or lower pluralhydric alcohol (as hereinbefore defined); a cross-linking agent and/or a denaturing agent for the gelatin being present at least when the synthetic organic detergent present is solely an anionic detergent and the liquid medium is aqueous.

2. An elastic detergent bar according to Claim 1 wherein the synthetic organic detergent is an anionic or an amphoteric synthetic organic detergent, the gelatin is a Type A gelatin of 100 to 300 g Bloom, a cross-linking agent and/or a denaturing agent is (or are) present, which cross-linking agent is a salt of aluminium, calcium, magnesium or zinc, and which denaturing agent is urea, and the liquid medium is water, the percentages of components being from 10% to 80% of synthetic organic detergent, from 5% to 30% of gelatin, from 0.1 to 5% of cross-linking agent and/or denaturing agent and from 5% to 60% of water.

3. An elastic detergent bar according to Claim 2 wherein the synthetic organic detergent is an anionic detergent.

4. An elastic detergent bar according to Claim 1 comprising from 10% to 80% of a mixture of anionic and amphoteric synthetic organic detergents in a proportion in the range from 1:5 to 5:1, from 5% to 30% of gelatin and from 5% to 60% of water.

5. An elastic detergent bar according to Claim 4 wherein the amphoteric synthetic organic detergent is an imidazolinium betaine or betainodipropionate or mixture thereof, the proportion of anionic to amphoteric synthetic organic detergent is in the range from 1:4 to 2:1 and the gelatin is a Type A gelatin and of 100 to 300 g Bloom.

6. An elastic detergent bar according to Claim 5 wherein the mixture of anionic and amphoteric synthetic organic detergents is from 35% to 70% of the bar, the amphoteric synthetic organic detergent is triethanolammonium 1-carboxymethyl-1-carboxy-ethoxyethyl-2-coco-imidazolinium betaine, the gelatin is of 200 to 300 g Bloom and is 7% to 25% of the bar and the liquid medium is 10% to 40% of the bar and comprises from 3% to 20% of lower pluralhydric alcohol.

7. An elastic detergent bar according to any of the preceding Claims which contains sufficient gas in small bubbles distributed throughout the bar so that the density of the bar is in the range from 0.5 to 0.98 g/cc.

8. An elastic detergent bar according to Claim 7 wherein the detergent constitutes from 20% to 80% of the bar and is a mixture of anionic and amphoteric synthetic organic detergents in a proportion in the range from 1:5 to 5:1, and which contains from 5% to 30% of gelatin and from 5% to 50% of water and wherein the gas is air.

9. An elastic detergent bar according to Claim 8 wherein the anionic synthetic organic detergent is an alkali metal higher fatty monoglyceride sulphate, an ammonium higher fatty monoglyceride sulphate, a triethanolammonium higher fatty alcohol sulphate or a mixture of any thereof, the amphoteric synthetic organic detergent is an imidazolinium betaine, a betaminodipropionate or a mixture thereof, the proportion of anionic synthetic organic detergent to amphoteric synthetic organic detergent is in the range from 1:3 to 3:1 the gelatin is a Type A gelatin of 100 to 300 g Bloom, and with density of the bar is in the range from 0.65 to 0.9 g/cc.
10. An elastic detergent bar according to Claim 1 which comprises a deterative quantity of synthetic organic detergent, a gelling and bodying content of gelatin and sufficient lower pluralhydric alcohol to act as a solvent and gelling medium for the detergent and gelatin, the proportions of the mentioned components being such as to produce a solid elastic detergent bar substantially free of water.
11. An elastic detergent bar according to Claim 10 which comprises from 10% to 70% of a synthetic organic detergent which is an ammonium or lower alkanolammonium anionic synthetic organic detergent or a mixture of such anionic synthetic organic detergent(s) and amphoteric synthetic organic detergent(s), from 8% to 35% of gelatin and from 20% to 65% of a lower pluralhydric alcohol, and which is free of water.
12. An elastic detergent bar according to Claim 11 wherein the synthetic organic detergent is a synthetic anionic organic detergent, the gelatin is a Type A gelatin of 100 to 300 g Bloom and the pluralhydric alcohol is a mixture of glycerol and propylene glycol in a ratio in the range from 5:1 to 1:2.
13. An elastic detergent bar substantially as described in any of the Examples.
14. A method for manufacturing an elastic detergent bar which comprises heating a mixture of a synthetic organic detergent, gelatin, a liquid medium which is water and/or lower pluralhydric alcohol (as hereinbefore defined) and, at least when the synthetic organic detergent is solely an anionic detergent and the liquid medium is aqueous, a cross-linking agent and/or a denaturing agent for the gelatin, and when water is present in the liquid medium, evaporating off a proportion of the water while the mix is in the liquid state, and forming the bar.
15. A method according to Claim 14 which comprises mixing the synthetic organic detergent, gelatin, and water as the liquid medium, to dissolve the gelatin therein, mixing an insoluble gas therewith to produce small bubbles throughout the mixture and to increase the volume thereof, and cooling the mix to solidify it and entrap the gas bubbles therein.
16. A method according to Claim 14 wherein the liquid medium includes a lower pluralhydric alcohol.
17. A method according to Claim 16 wherein the pluralhydric alcohol is a mixture of propylene glycol and glycerol and the detergent bar made is free of water.
18. A method for manufacturing an elastic detergent bar substantially as described in any of the Examples.
19. An elastic detergent bar which has been manufactured by a method according to any of Claims 14 to 17.

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